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GLASS FORMING RANGES OF AMORPHOUS ALLOYS*

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Two main methods of synthesis of amorphous metallic alloys are based on the rapid solidification (RS) of molten alloys and on isothermal solid state reactions (SSR) between pure metals. We discuss recent calculations for the glass forming range for both techniques and we compare the predicted homogeneity ranges of the amorphous phase with experiments.

1. Introduction

Since 1960, amorphous metallic alloys have been prepared by the RS of melts [1]. In general, the faster the cooling rate, the wider is the homogeneity range of the amorphous phase. Although cooling rates as high as 10^{12} K/s can be achieved following surface melting by pico-second duration laser pulses, the cooling rates used by industry rarely exceed 10^6 K/s. At cooling rates of 10^6 K/s, the glass forming range (GFR) of rapidly solidified metallic melts usually consists of a few finite composition ranges centered near the composition of deep eutectics.

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Since 1983, amorphous metallic alloys have also been produced by SSRs between pairs of metals that have a large negative heat of mixing [2]. Although most of the binary metallic systems that form amorphous alloys by the RS method also form amorphous alloys by the SSR method, the GFR of the two methods are quite different. Contrary to the RS method, the GFR for the SSR method is continuous in composition. This range is mainly determined by metastable-equilibrium thermodynamics and depends only weakly on the reaction temperature. In this paper we describe the calculations for the GFRs for the two methods of synthesis noting their similarities and differences. The comparison is done for the Ni-Ti system because sufficient experimental data are available for both synthesis methods.

2. Glass Forming Range for Rapidly Solidified Melts

The formation of glassy alloy by the RS method requires avoiding the crystallization of the undercooled melt. Experience has shown that during the fast cooling of alloy melt, polymorphous crystallization is favored over solidification involving solute partitioning. Thus, if polymorphous crystallization is avoided while the melt temperature is decreased to below the glass-transition temperature, T_g , the alloy will be trapped in the glassy state. For binary alloys the thermodynamic transformation temperature for partitionless crystallization can be described by a T_0 curve which is the temperature-composition locus at which the driving force for the transformation is zero. Recently, Nash and the author [3] calculated the volume fraction of partitionlessly crystallized material during continuous cooling of molten $Ni_{1-x}Ti_x$ alloy as a function of cooling rate and alloy composition, x . We derived an expression for the

thermodynamic force for crystallization, ΔG , as a function of temperature and alloy composition from a thermodynamic model [4] that was fitted to the equilibrium phase diagram of the Ni-Ti system. We used the classical theory of homogeneous nucleation to predict the nucleation rate per unit volume of undercooled melt. We integrated numerically the nucleation rate to calculate the total volume fraction of crystal, $\zeta(T, x, dT/dt)$, formed during continuous cooling from T_0 to T as a function of alloy composition and cooling rate. We defined, arbitrarily, a crystalline volume fraction $\zeta < 10^{-6}$ as a criterion for retention of the glassy state. We used these results to calculate the composition dependence of the temperature $T'(x, \zeta, dT/dt)$ at which a volume fraction $\zeta = 10^{-6}$ of crystalline terminal solid solution has been formed by polymorphous crystallization during continuous cooling at the rate $dT/dt = 10^6$ K/s. The solid curves in Fig. 1 show the T' curves while the ^{dash-}_Λ dotted curves are the T_0 curves calculated from the same thermodynamic model. The solid triangles in Fig. 1 are the T' -values for the three equilibrium intermetallics in the Ni-Ti system, Ni_3Ti , $NiTi$, and $NiTi_2$. The thermodynamic model we have used for Ni-Ti assumes that the intermetallic phases are line compounds and hence we do not have the variation of free energy as a function of composition away from the stoichiometric compositions. The dashed curves are our estimate of the T' curves for the compounds; these are inverted parabolas that pass through the single calculated T' points (solid triangles) and have a width of $\Delta x = 0.06$ at $T = T_x$.

In the present model, the GFR is determined by the intersection of the T' curves with the $T_g(x)$ curve. This criterion states that for those alloy compositions for which $T' < T_g$, as the temperature of the molten alloy is lowered, the alloy will become trapped in the glassy state before

it has a chance to crystallize. We do not have measurements of T_g in amorphous $Ni_{1-x}Ti_x$ alloys and we thus assume that the T_x measurements give a good estimate of T_g . The solid circles in Fig. 1 are a compilation of T_x measurements in amorphous $Ni_{1-x}Ti_x$ alloys prepared by the RS of melts [5]. The calculations are in good agreement with the measurements. In particular, the model predicts the difficulty in synthesizing amorphous alloys by rapidly quenching melts with compositions close to the intermetallics $NiTi$ and Ni_3Ti .

3. Glass Forming Range for Solid State Reactions

Schwarz and Johnson [2] showed that the homogeneity range of amorphous $Au_{1-x}La_x$ alloy formed by a SSR between thin films of gold and lanthanum equals the range predicted by a metastable free-energy diagram evaluated at the reaction temperature. Since this work, metastable free-energy diagrams have been shown to predict not only the phases and compositions of SSRs in thin films, but also the composition ranges of metastable phases (amorphous and crystalline) produced by mechanically alloying mixtures of pure metal powders. In fact, this agreement supports the thesis [6] that the synthesis of amorphous alloy powders by mechanical alloying occurs by a SSR similar to that responsible for the amorphization of thin-film multilayers.

The metastable free-energy diagram must include curves for the crystalline terminal solutions, the amorphous alloy, and the crystalline intermetallics, all evaluated at the reaction temperature. Two methods have been used to evaluate the free energy diagrams. In the quasichemical approach, first used in [2], the free energy of the amorphous phase is calculated by regular solution theory using a measured, or an empirically

calculated enthalpy of mixing. The phase stabilities of the pure elements and of the intermetallic compounds are estimated from the known heats of fusion. In the thermodynamic modeling approach, first used by Saunders and Miodownik [7] the free energy of all the phases are obtained from a thermodynamic model that is numerically fitted to the measured phase equilibrium data.

Figure 2 shows the free energy diagram for Ni-Ti system evaluated at 240 K [6]. We used the thermodynamic model of Murray [4] to determine the free-energy curves for the terminal solid solutions (thin-trace curves). We determined the difference ΔG^{a-x} for the pure elements by modifying the linear approximation for ΔG^{a-x} [8] to take into account excess specific heat measurements in undercooled liquids. We calculated the free energy of the amorphous alloy (heavy-trace curve) using Miedema's modified regular solution theory [9]. The common tangents to the free energy curves for the amorphous phase and the terminal solutions (dashed lines) predicts the GFR for $Ni_{1-x}Ti_x$ prepared by the SSR method to be continuous for $0.3 < x < 0.7$. This prediction, as well as the homogeneity ranges of the two-phase products, are in excellent agreement with the products obtained by mechanically alloying pure Ni and Ti powders, which are denoted by the filled (single phase amorphous) and half-filled (amorphous plus terminal solid-solution phase) circles near the bottom of Fig.2. The diagram also predicts an extended metastable Ni-rich solid solution (regime (a) in Fig. 2) which is observed [6].

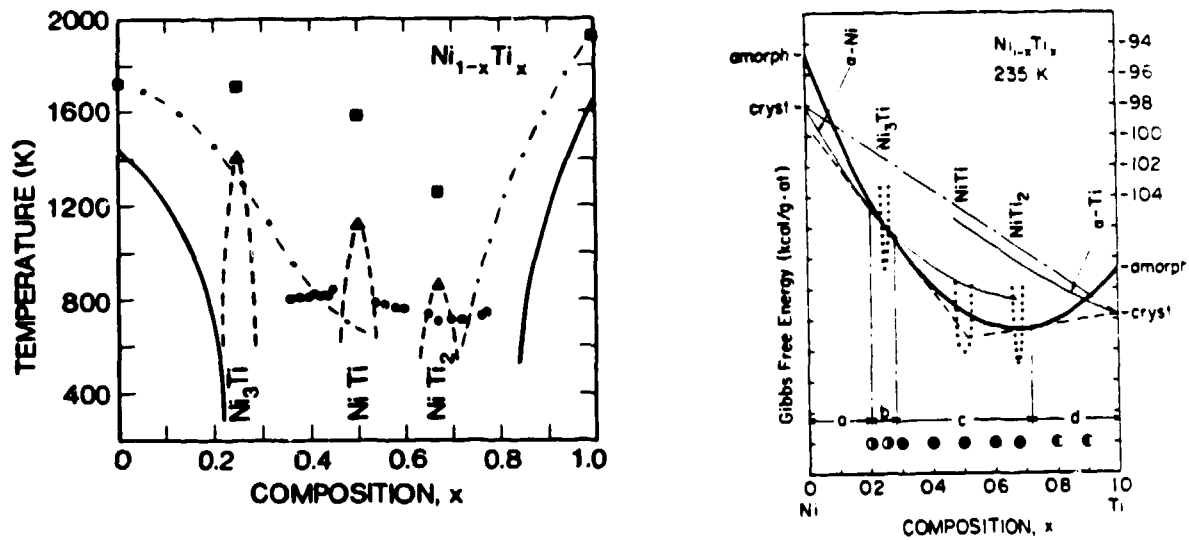


Fig. 1 (left) T' versus composition, x , curves for the terminal solutions (solid curves) and intermetallic compounds (dash curves) of rapidly solidified Ni-Ti evaluated for a volume fraction $\zeta = 10^{-6}$ of crystalline material and cooling rate of 10^6 K/s. The squares are equilibrium melting temperatures of the pure metals and the compounds.

Fig. 2 (right) Free energy diagram for the Ni-Ti system evaluated at 235 K. The common tangents (dash lines) to the crystalline solid solutions and the amorphous phase (heavy trace curve) define the composition regimes (a)=nickel-rich terminal solution, (b)=mixture of terminal solution and amorphous alloy, (c)=single-phase amorphous, and (d)=mixture of amorphous alloy and titanium-rich terminal solution.

4. Discussion

Our understanding of the thermodynamic and kinetic processes during the RS of melts and SSRs has matured enough to allow us to predict, for both methods, GFRs that are closed to those measured. The predicted GFRs for the two techniques show clear differences. For the RS technique, the GFR is discontinuous because it is difficult to avoid the polymorphous crystallization of the undercooled melt at compositions near those of crystalline intermetallics. In particular, Fig. 1 shows that amorphous $\text{Ni}_{1-x}\text{Ti}_x$ with $x \approx 0.25$ and $x \approx 0.5$ cannot be formed by RS at cooling rates of the order of 10^6 K/s. On the other hand, the GFR for the SSR method is continuous from $x = 0.3$ to $x = 0.7$.

The $T'(x)$ diagram for $\text{Ni}_{1-x}\text{Ti}_x$ in Fig. 1 predicts the gaps in the GFR of Ni-Ti for compositions near the intermetallics Ni_3Ti and NiTi . It also predicts a gap near NiTi_2 , contrary to observation. A possible reason for this discrepancy, having to do with chemical short range order in the liquid, was discussed in [3]. Another possible explanation is that the thermodynamic model for Ni-Ti overestimates the value of the driving force for crystallization, $\Delta G(x, T)$. The overestimate may arise because the thermodynamic model does not take into account the increase in the specific heat of the undercooled melt in the regime $T_m - T_g$. A smaller ΔG would result in lower T' values.

Free-energy diagrams that predict quantitatively the homogeneity ranges of the SSR products are difficult to construct. For the quasichemical method we need to know the difference Δc_p^{a-x} between the specific heats of the two pure metals in the (hypothetical) amorphous and crystalline states in the temperature regime $T_g - T_m$. This difference

allows us to calculate the corresponding difference in free energy ΔG^{a-x} . The approximation $\Delta c_p^{a-x} = 0$ gives the linear temperature dependence $\Delta G^{a-x} = \Delta H^f(T_m - T)/T_m$, where ΔH^f is the heat of fusion [8]. Although this approximation is adequate for binary systems with very large negative heats of mixing [2], in most other cases using the linear approximation causes us to underestimate the stability of the amorphous phase and this results in a predicted GFR that is narrower than observed. A similar problem affects the thermodynamic model approach. In this case the simple extrapolation to low temperatures of the polynomial in composition and temperature that describe the molten alloy result in a glassy phase that is too stable. The error arises because the current thermodynamic models do not include Δc_p^{a-x} . In conclusion, neither the quasichemical nor the thermodynamic modeling approaches give metastable free-energy diagrams that describe quantitatively the products of SSRs. The best solution to date is to use either method to construct an approximate free energy diagram and to then estimate the increase in the stability of the amorphous phase to take into account the difference in specific heats, Δc_p^{a-x} . This correction may be done using thermodynamic models for Δc_p^{a-x} , as done in [4], or using direct measurements of the electrochemical potentials of the pure metals in the amorphous phase, as recently demonstrated by Bormann et al. [10].

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